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## Liquid–Liquid Equilibria of Ionic Liquids–Water–Acetic Acid Mixtures

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## **Supporting Information**

### **Liquid-Liquid Equilibria of Ionic Liquids-Water-Acetic Acid Mixtures**

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**Table S1.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + MTBE) at 293.15 K and 313.15 K and at 101 kPa. The mole fractions of water, acetic acid and MTBE are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			MTBE-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
$T = 293.15 \text{ K}$								
0.9890	0.0000	0.0110	0.0566	0.0000	0.9434	-	-	-
0.9739	0.0150	0.0111	0.1146	0.0643	0.8211	1.06	4.29	36.43
0.9397	0.0474	0.0129	0.2032	0.1532	0.6436	0.97	3.23	14.95
0.9246	0.0601	0.0153	0.3094	0.2041	0.4865	1.21	3.40	10.15
0.9077	0.0748	0.0175	0.3852	0.2151	0.3997	1.17	2.88	6.78
0.8943	0.0871	0.0186	0.4252	0.2181	0.3567	1.10	2.50	5.27
0.8864	0.0917	0.0219	0.4587	0.2180	0.3233	1.12	2.38	4.59
0.8798	0.0970	0.0232	0.4985	0.2177	0.2838	1.13	2.24	3.96
0.8398	0.1256	0.0346	0.5396	0.2195	0.2409	1.02	1.75	2.72
0.8280	0.1329	0.0391	0.5639	0.2200	0.2161	1.03	1.66	2.43
$T = 313.15 \text{ K}$								
0.9931	0.0000	0.0069	0.0466	0.0000	0.9534	-	-	-
0.9850	0.0075	0.0075	0.0674	0.0305	0.9021	0.93	4.07	59.43
0.9530	0.0394	0.0076	0.2098	0.1404	0.6498	1.04	3.56	16.19
0.9518	0.0397	0.0085	0.1794	0.1330	0.6876	0.95	3.35	17.77
0.9260	0.0582	0.0158	0.3071	0.1880	0.5049	1.14	3.23	9.74
0.8966	0.0845	0.0189	0.4786	0.2334	0.2880	1.32	2.76	5.17
0.8586	0.1121	0.0293	0.5652	0.2408	0.1940	1.28	2.15	3.26
0.8267	0.1331	0.0402	0.6127	0.2351	0.1522	1.21	1.77	2.38

$u(x_i) = 0.01$ ;  $u(T) = 0.5 \text{ K}$ ;  $u(p) = 2 \text{ kPa}$ .

**Table S2.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + MIBK) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and MIBK are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			MIBK-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
$T = 293.15$ K								
1.0000	0.0000	0.0000	0.0991	0.0000	0.9009	-	-	-
0.9697	0.0267	0.0036	0.1667	0.0758	0.7575	0.66	2.84	16.51
0.9630	0.0330	0.0040	0.2081	0.1208	0.6711	0.92	3.66	16.94
0.9361	0.0560	0.0079	0.2973	0.1622	0.5405	0.88	2.90	9.12
0.9138	0.0777	0.0085	0.3680	0.1991	0.4329	0.91	2.56	6.36
0.9072	0.0839	0.0089	0.4151	0.2075	0.3774	0.95	2.47	5.41
0.8921	0.0950	0.0129	0.4516	0.2258	0.3226	1.02	2.38	4.70
0.8877	0.0996	0.0127	0.4813	0.2305	0.2882	1.05	2.31	4.27
0.8618	0.1200	0.0182	0.5226	0.2261	0.2513	0.96	1.88	3.11
0.8560	0.1320	0.0120	0.5727	0.2238	0.2035	0.94	1.70	2.53
0.7800	0.1650	0.0550	0.6936	0.1908	0.1156	0.96	1.16	1.30

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

**Table S3.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [P<sub>666 14</sub>]Cl) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [P<sub>666 14</sub>]Cl are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
1.000	0.000	0.000	0.826	0.000	0.174	-	-	-
0.998	0.002	0.000	0.497	0.112	0.391	4.64	56.00	112.45
0.998	0.002	0.000	0.499	0.046	0.455	1.68	23.00	46.00
0.995	0.005	0.000	0.496	0.080	0.424	1.25	16.00	32.10
0.992	0.008	0.000	0.499	0.073	0.428	0.71	9.13	18.14
0.984	0.016	0.000	0.471	0.277	0.252	2.07	17.31	36.17
0.980	0.020	0.000	0.490	0.235	0.275	1.34	11.75	23.50
0.920	0.080	0.000	0.498	0.377	0.125	1.04	4.71	8.71
0.883	0.117	0.000	0.470	0.345	0.185	0.54	2.95	5.54
0.833	0.167	0.000	0.481	0.384	0.135	0.57	2.30	3.98
0.833	0.167	0.000	0.530	0.360	0.110	0.61	2.16	3.39
0.824	0.176	0.000	0.521	0.385	0.094	0.68	2.19	3.46
0.820	0.180	0.000	0.510	0.394	0.096	0.68	2.19	3.52
0.811	0.189	0.000	0.527	0.390	0.083	0.70	2.06	3.18
0.806	0.194	0.000	0.519	0.391	0.090	0.66	2.02	3.13
0.789	0.211	0.000	0.494	0.395	0.111	0.56	1.87	2.99
0.773	0.227	0.000	0.509	0.411	0.080	0.66	1.81	2.75
0.758	0.241	0.001	0.502	0.410	0.088	0.61	1.70	2.57
0.749	0.250	0.001	0.540	0.388	0.072	0.64	1.55	2.15
0.728	0.272	0.000	0.520	0.413	0.067	0.65	1.52	2.13
0.714	0.286	0.000	0.525	0.420	0.055	0.70	1.47	2.00
0.698	0.302	0.000	0.544	0.399	0.057	0.64	1.32	1.70

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

In the case of the (water + [P<sub>666,14</sub>]Cl) binary system, a formation of an emulsion within the addition of water to this phosphonium-based ionic liquid was observed. This observation is in agreement with that already reported into the literature.<sup>1,2</sup>

**Table S4.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [P<sub>666,14</sub>][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [P<sub>666,14</sub>][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
1.000	0.000	0.000	0.127	0.000	0.873	-	-	-
0.958	0.042	0.000	0.298	0.070	0.632	0.07	1.67	5.36
0.943	0.057	0.000	0.309	0.081	0.610	0.06	1.42	4.34
0.902	0.098	0.000	0.354	0.118	0.528	0.06	1.20	3.07
0.892	0.108	0.000	0.355	0.121	0.524	0.06	1.12	2.82
0.867	0.133	0.000	0.420	0.147	0.433	0.08	1.11	2.28

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

In the case of the (water + [P<sub>666,14</sub>][NTf<sub>2</sub>]) binary system, a formation of an emulsion within the addition of water to this phosphonium-based ionic liquid was observed. This observation is in agreement with that already reported into the literature in the case of the [P<sub>666 14</sub>]Cl.<sup>1,2</sup>

**Table S5.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [C<sub>2</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C<sub>2</sub>mim][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
0.9995	0.0000	0.0005	0.2954	0.0000	0.7046	-	-	-
0.9836	0.0139	0.0025	0.2342	0.0285	0.7373	0.14	2.05	8.61
0.9758	0.0217	0.0025	0.2164	0.0478	0.7358	0.15	2.20	9.93
0.9439	0.0538	0.0023	0.2952	0.1253	0.5795	0.21	2.33	7.45
0.9400	0.0577	0.0023	0.2965	0.1358	0.5677	0.21	2.35	7.46
0.9368	0.0606	0.0026	0.3072	0.1407	0.5521	0.22	2.32	7.08
0.9251	0.0720	0.0029	0.3685	0.1545	0.4770	0.23	2.15	5.39
0.9075	0.0892	0.0033	0.3957	0.1920	0.4123	0.28	2.15	4.94
0.8697	0.1249	0.0054	0.4827	0.2282	0.2891	0.34	1.83	3.29
0.8569	0.1363	0.0068	0.5133	0.2355	0.2512	0.37	1.73	2.88

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

**Table S6.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [C<sub>4</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C<sub>4</sub>mim][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
0.9995	0.0000	0.0005	0.2400	0.0000	0.7600	-	-	-
0.9945	0.0049	0.0006	0.2478	0.0178	0.7344	0.21	3.63	14.58
0.9835	0.0160	0.0005	0.2614	0.0414	0.6972	0.16	2.59	9.74
0.9690	0.0303	0.0007	0.3001	0.0700	0.6299	0.17	2.31	7.46
0.9301	0.0685	0.0014	0.3499	0.1200	0.5301	0.16	1.75	4.66
0.9086	0.0909	0.0005	0.4131	0.1697	0.4172	0.21	1.87	4.11
0.9014	0.0964	0.0022	0.4223	0.1756	0.4021	0.22	1.82	3.89
0.9013	0.0961	0.0026	0.4144	0.1713	0.4143	0.22	1.78	3.88
0.9009	0.0961	0.0030	0.4091	0.1777	0.4132	0.22	1.85	4.07
0.8793	0.1172	0.0035	0.4337	0.2048	0.3615	0.25	1.75	3.54
0.8694	0.1275	0.0031	0.4627	0.2267	0.3106	0.29	1.78	3.34
0.8582	0.1373	0.0045	0.4688	0.2247	0.3065	0.28	1.64	3.00
0.8090	0.1840	0.0070	0.5090	0.2370	0.2540	0.28	1.29	2.05

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.



**Table S7.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [C<sub>4</sub>mmim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C<sub>4</sub>mmim][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
0.9996	0.0000	0.0004	0.1735	0.0000	0.8265	-	-	-
0.9984	0.0012	0.0004	0.1764	0.0073	0.8163	0.31	6.08	34.43
0.9813	0.0183	0.0004	0.2096	0.0419	0.7485	0.13	2.29	10.72
0.9635	0.0361	0.0004	0.2209	0.0665	0.7126	0.11	1.84	8.03
0.9539	0.0455	0.0006	0.2476	0.0828	0.6696	0.12	1.82	7.02
0.9290	0.0705	0.0005	0.2802	0.1143	0.6055	0.13	1.62	5.38
0.9085	0.0909	0.0006	0.331	0.1517	0.5173	0.15	1.67	4.58
0.8970	0.1017	0.0013	0.354	0.1801	0.4659	0.18	1.77	4.49
0.8603	0.1376	0.0021	0.4129	0.2217	0.3654	0.22	1.61	3.36
0.8263	0.1707	0.0030	0.4584	0.2472	0.2944	0.25	1.45	2.61

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

**Table S8.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [C<sub>6</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C<sub>6</sub>mim][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
0.9998	0.0000	0.0002	0.1968	0.0000	0.8032	-	-	-
0.9941	0.0057	0.0002	0.2129	0.0329	0.7542	0.31	5.77	26.95
0.9753	0.0244	0.0003	0.2410	0.0655	0.6935	0.16	2.68	10.86
0.9706	0.0290	0.0004	0.2513	0.0805	0.6682	0.17	2.78	10.72
0.9453	0.0538	0.0009	0.2607	0.1111	0.6282	0.15	2.07	7.49
0.9392	0.0600	0.0008	0.2743	0.1207	0.6050	0.15	2.01	6.89
0.9193	0.0799	0.0008	0.2978	0.1506	0.5516	0.16	1.88	5.82
0.9090	0.0901	0.0009	0.3350	0.1798	0.4852	0.19	2.00	5.41
0.8993	0.1001	0.0006	0.3538	0.1868	0.4594	0.19	1.87	4.74
0.8882	0.1109	0.0009	0.3629	0.1995	0.4376	0.19	1.80	4.40
0.8713	0.1279	0.0008	0.3855	0.2131	0.4014	0.20	1.67	3.77
0.8444	0.1547	0.0009	0.4200	0.2479	0.3321	0.23	1.60	3.22
0.8401	0.1589	0.0010	0.4401	0.2575	0.3024	0.26	1.62	3.09
0.8268	0.1716	0.0016	0.4460	0.2699	0.2841	0.27	1.57	2.92
0.8157	0.1824	0.0019	0.4579	0.2750	0.2671	0.28	1.51	2.69
0.7806	0.2173	0.0021	0.5102	0.2801	0.2097	0.30	1.29	1.97

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

**Table S9.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [C<sub>8</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C<sub>8</sub>mim][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
0.9996	0.0000	0.0004	0.1759	0.0000	0.8241	-	-	-
0.9921	0.0075	0.0004	0.1859	0.0335	0.7806	0.22	4.47	23.84
0.9872	0.0124	0.0004	0.1913	0.0432	0.7655	0.18	3.48	17.98
0.9715	0.0281	0.0004	0.2247	0.0964	0.6789	0.20	3.43	14.83
0.9543	0.0453	0.0004	0.2587	0.1456	0.5957	0.22	3.21	11.86
0.9194	0.0797	0.0009	0.3341	0.2153	0.4506	0.25	2.70	7.43
0.8619	0.1375	0.0006	0.3914	0.2637	0.3449	0.25	1.92	4.22
0.8525	0.1470	0.0005	0.3940	0.2643	0.3417	0.24	1.80	3.89
0.8490	0.1501	0.0009	0.3973	0.2691	0.3336	0.24	1.79	3.83
0.8051	0.1932	0.0017	0.4573	0.2951	0.2476	0.29	1.53	2.69

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

**Table S10.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [C<sub>10</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C<sub>10</sub>mim][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
0.9998	0.0000	0.0002	0.1526	0.0000	0.8474	-	-	-
0.9934	0.0064	0.0002	0.1592	0.0353	0.8055	0.25	5.52	34.42
0.9823	0.0175	0.0002	0.1976	0.0872	0.7152	0.25	4.98	24.77
0.9622	0.0375	0.0003	0.2115	0.1017	0.6868	0.15	2.71	12.34
0.9004	0.0993	0.0003	0.2367	0.1825	0.5808	0.13	1.84	6.99
0.8567	0.1430	0.0003	0.3001	0.2414	0.4585	0.16	1.69	4.82
0.8177	0.1820	0.0003	0.3718	0.2917	0.3365	0.21	1.60	3.52
0.7979	0.2018	0.0003	0.3953	0.3063	0.2984	0.23	1.52	3.06
0.7345	0.2652	0.0003	0.4502	0.3209	0.2289	0.25	1.21	1.97

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

**Table S11.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [C<sub>4</sub>mpyrr][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [C<sub>4</sub>mpyrr][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
1.0000	0.0000	0.0000	0.2194	0.0000	0.7806	-	-	-
0.9767	0.0233	0.0000	0.1681	0.0609	0.7710	0.15	2.61	15.19
0.9638	0.0362	0.0000	0.1760	0.0810	0.7430	0.14	2.24	12.25
0.9396	0.0604	0.0000	0.2028	0.1248	0.6724	0.14	2.07	9.57
0.9226	0.0771	0.0003	0.2685	0.1500	0.5815	0.16	1.95	6.69
0.9081	0.0916	0.0003	0.2996	0.1650	0.5354	0.16	1.80	5.46
0.8927	0.1066	0.0007	0.3011	0.1948	0.5041	0.18	1.83	5.42
0.8542	0.1444	0.0014	0.3584	0.2350	0.4066	0.21	1.63	3.88
0.8193	0.1777	0.0030	0.3724	0.2769	0.3507	0.24	1.56	3.43

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

**Table S12.** Composition of the experimental tie-line ends, and values of the solute distribution ratios ( $\beta_x$  and  $\beta_w$  calculated from the mole and mass fractions, respectively) and selectivity ( $S$ ) for the ternary system (water + acetic acid + [N<sub>1114</sub>][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa. The mole fractions of water, acetic acid and [N<sub>1114</sub>][NTf<sub>2</sub>] are represented by  $x_1$ ,  $x_2$  and  $x_3$ , respectively.

Water-rich phase			Ionic Liquid-rich phase			$\beta_w$	$\beta_x$	$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$			
1.000	0.000	0.000	0.230	0.000	0.770	-	-	-
0.989	0.011	0.000	0.283	0.042	0.675	0.26	3.82	13.34
0.978	0.022	0.000	0.296	0.046	0.658	0.15	2.09	6.91
0.969	0.031	0.000	0.296	0.061	0.643	0.14	1.97	6.44
0.957	0.043	0.000	0.319	0.078	0.603	0.14	1.81	5.44
0.954	0.046	0.000	0.317	0.085	0.598	0.15	1.85	5.56
0.951	0.049	0.000	0.344	0.092	0.564	0.16	1.88	5.19
0.911	0.089	0.000	0.403	0.145	0.452	0.18	1.63	3.68
0.875	0.125	0.000	0.451	0.199	0.350	0.23	1.59	3.09
0.824	0.176	0.000	0.526	0.245	0.229	0.31	1.39	2.18

$u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa.

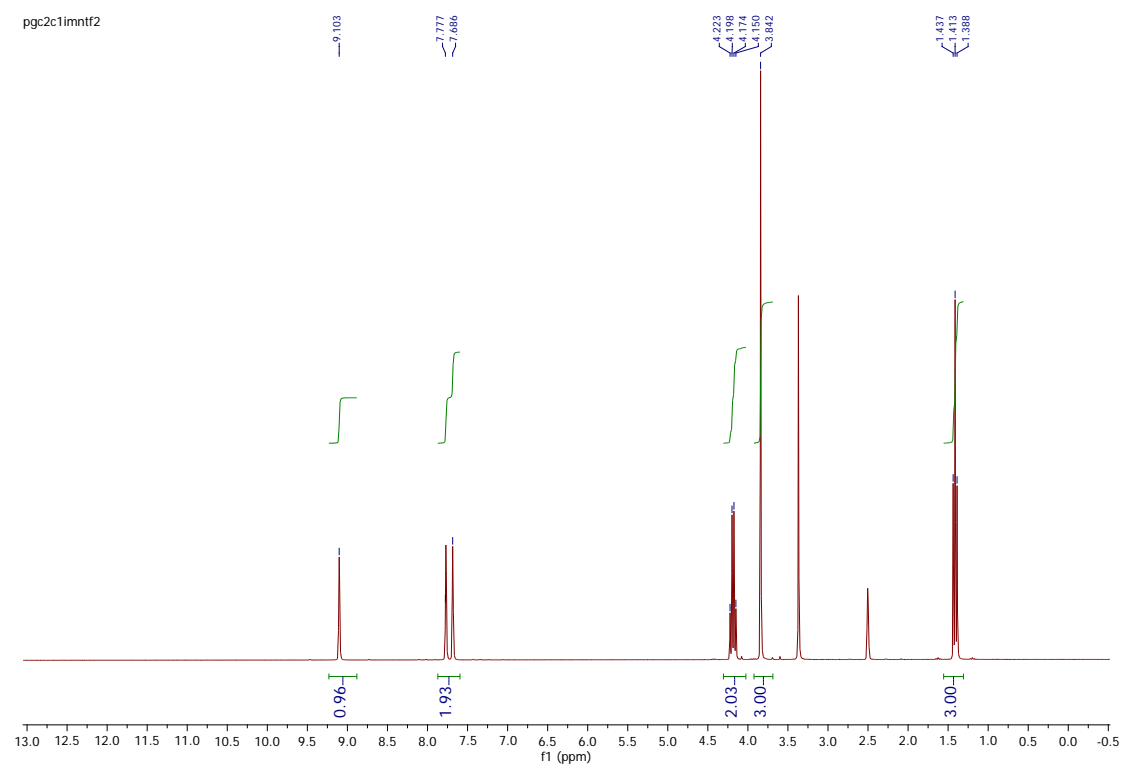
**Table S13.** Relative deviation between experimental water solubility in IL data reported herein with published data expressed in water mole fraction in IL,  $x_1$  at 101 kPa.

IL	This work <sup>a</sup>	$x_1$ Literature data	Relative Deviation (%)
[P <sub>66614</sub> ][Cl]	0.8261	0.814 <sup>b</sup> [3]	1.49
		0.818 <sup>c</sup> [4]	0.99
		0.829 <sup>c</sup> [5]	-0.35
		0.824 <sup>c</sup> [6]	0.25
[P <sub>66614</sub> ][NTf <sub>2</sub> ]	0.1206	0.081 <sup>b</sup> [3]	48.9
		0.088 <sup>c</sup> [4]	37.1
		0.230 <sup>c</sup> [6]	-47.6
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	0.2954	0.2357 <sup>b</sup> [7]	25.3
		0.2869 <sup>b</sup> [8]	2.96
		0.31 <sup>d</sup> [9]	-4.71
		0.2970 <sup>e</sup> [10]	-0.54
		0.3050 <sup>d</sup> [11]	-3.15
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	0.2400	0.2484 <sup>b</sup> [7]	-3.38
		0.2443 <sup>b</sup> [8]	-1.76
		0.27 <sup>d</sup> [9]	-11.1
		0.2431 <sup>f</sup> [10]	-1.28
		0.3210 <sup>d</sup> [11]	-25.2
		0.2931 <sup>b</sup> [12]	-18.1
[C <sub>4</sub> mmim][NTf <sub>2</sub> ]	0.1735	-	
[C <sub>6</sub> mim][NTf <sub>2</sub> ]	0.1968	0.1978 <sup>b</sup> [8]	-0.51
		0.2703 <sup>b</sup> [12]	-27.2
		0.2117 <sup>g</sup> [13]	-7.04
[C <sub>8</sub> mim][NTf <sub>2</sub> ]	0.1759	0.1781 <sup>b</sup> [8]	-1.24
		0.2411 <sup>b</sup> [12]	-27.0
		0.1951 <sup>g</sup> [13]	-9.84
[C <sub>10</sub> mim][NTf <sub>2</sub> ]	0.1526	-	
[C <sub>4</sub> mpyrr][NTf <sub>2</sub> ]	0.2194	0.2260 <sup>h</sup> [10]	-2.92
		0.199 <sup>b</sup> [14]	10.3
[N <sub>1114</sub> ][NTf <sub>2</sub> ]	0.2300	0.2043 <sup>i</sup> [10]	12.6
		0.2420 <sup>d</sup> [11]	-4.96

<sup>a</sup> This work at 293.15 K:  $u(x_i) = 0.01$ ;  $u(T) = 0.5$  K;  $u(p) = 2$  kPa. <sup>b</sup> at 293.15 K. <sup>c</sup> at 298.15 K.

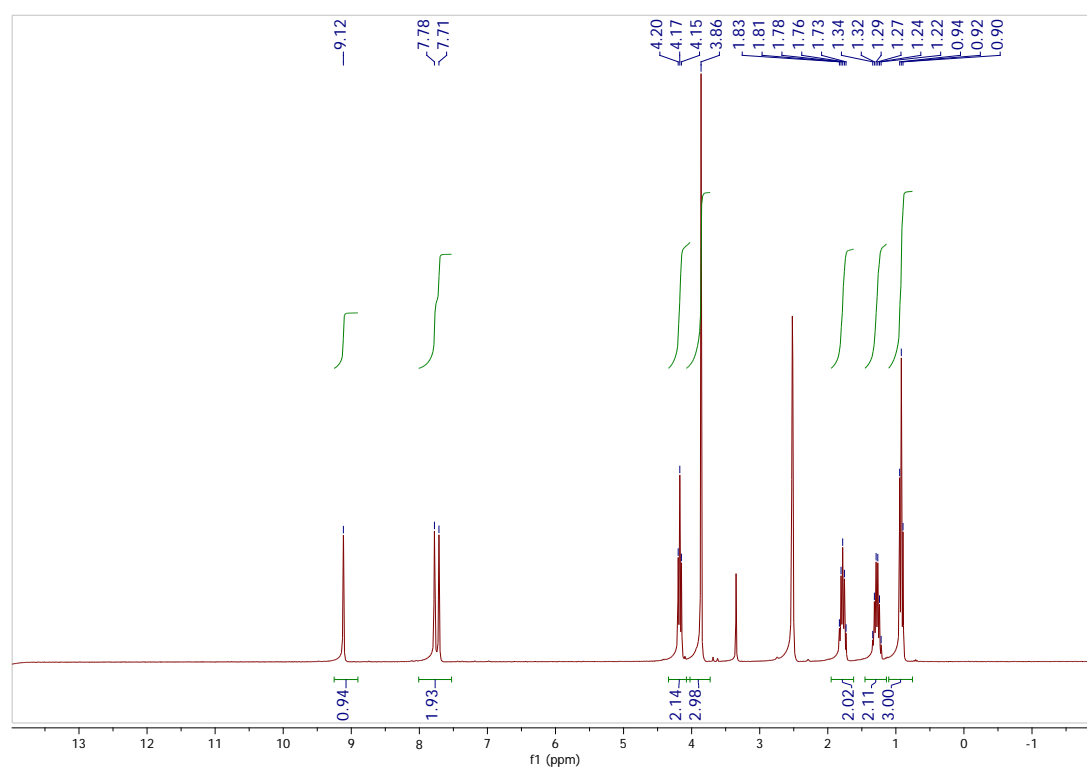
<sup>d</sup> at room temperature. <sup>e</sup> at 292.62 K. <sup>f</sup> at 290.13 K. <sup>g</sup> at 296.65 K. <sup>h</sup> at 290.35 K. <sup>i</sup> at 289.15 K.

**Figure S1.**  $^1\text{H}$ -NMR of  $[\text{C}_2\text{mim}][\text{NTf}_2]$  in  $\text{d}_6$ -DMSO.

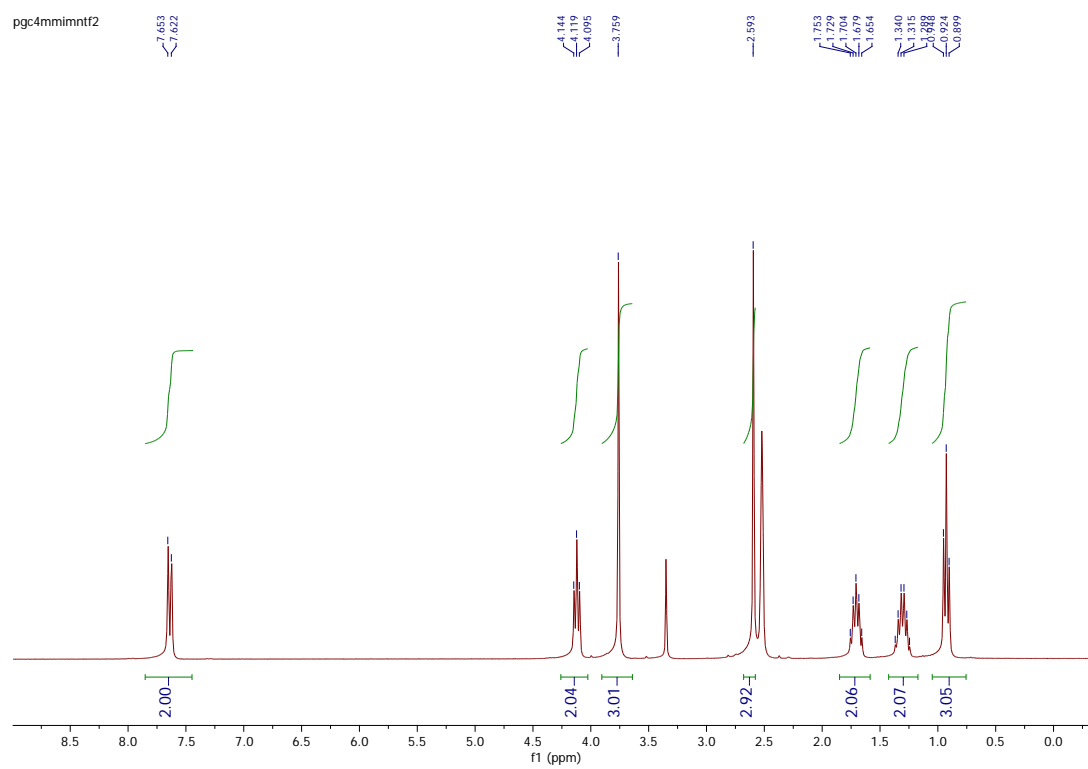




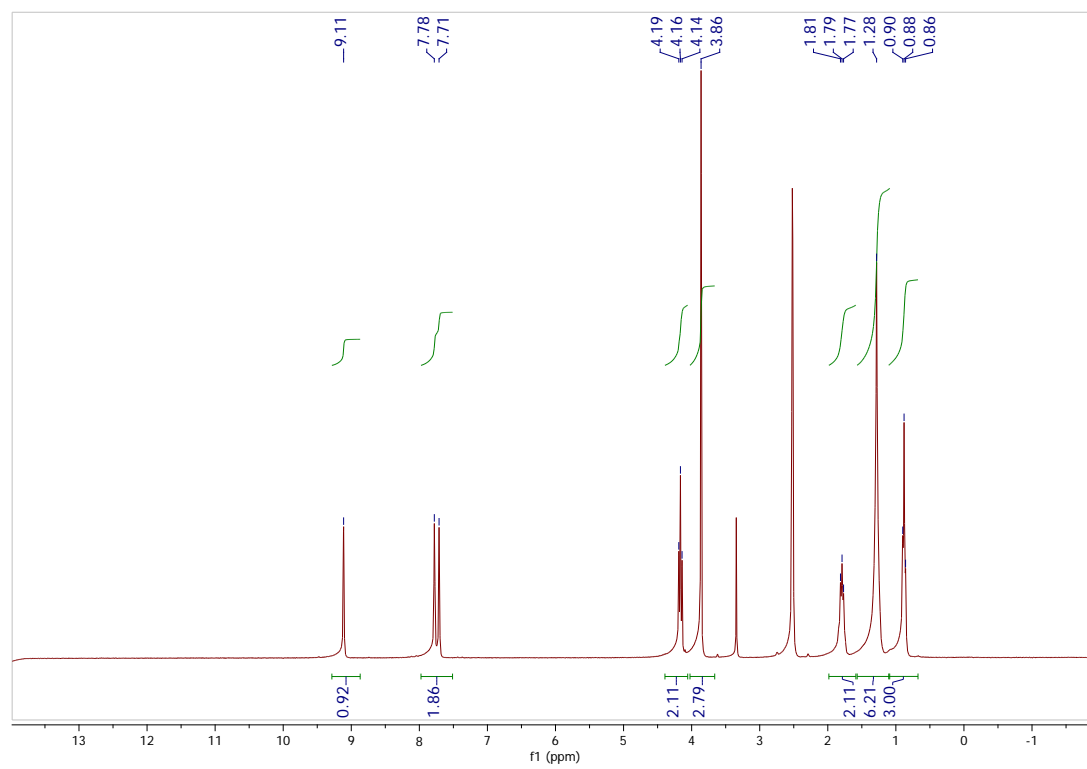
**Figure S2.**  $^1\text{H}$ -NMR of  $[\text{C}_4\text{mim}][\text{NTf}_2]$  in  $\text{d}_6$ -DMSO.



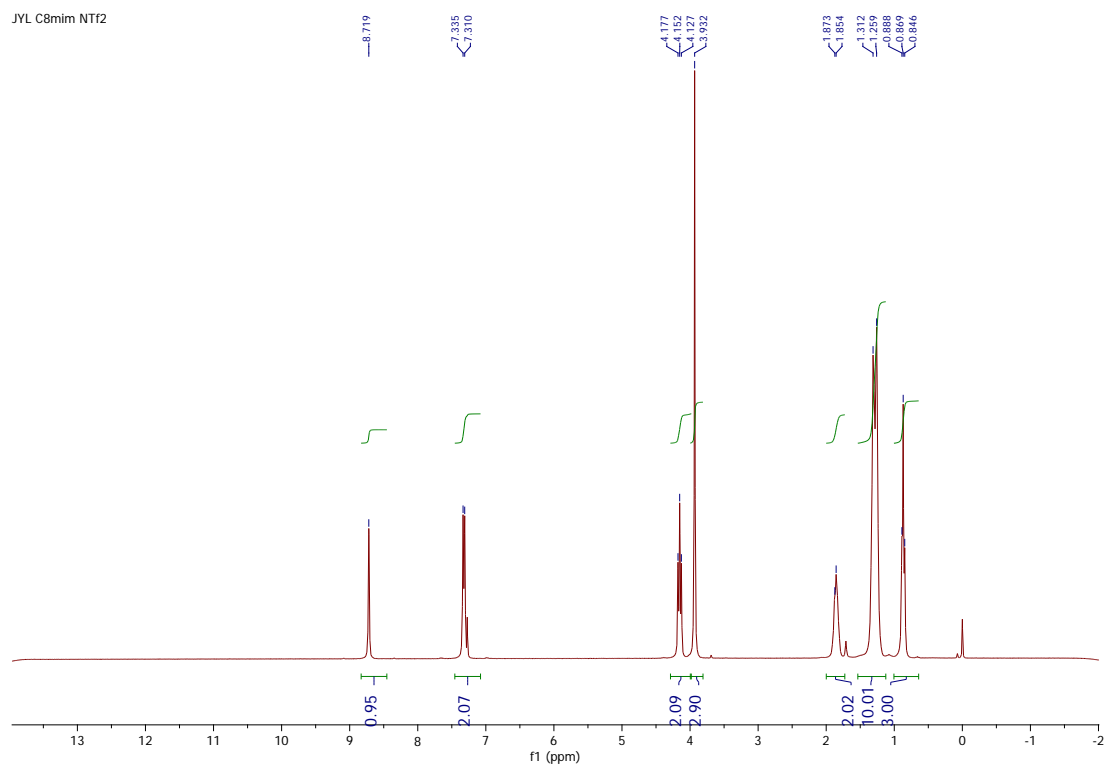
**Figure S3.**  $^1\text{H}$ -NMR of  $[\text{C}_4\text{mmim}][\text{NTf}_2]$  in  $\text{d}_6$ -DMSO.



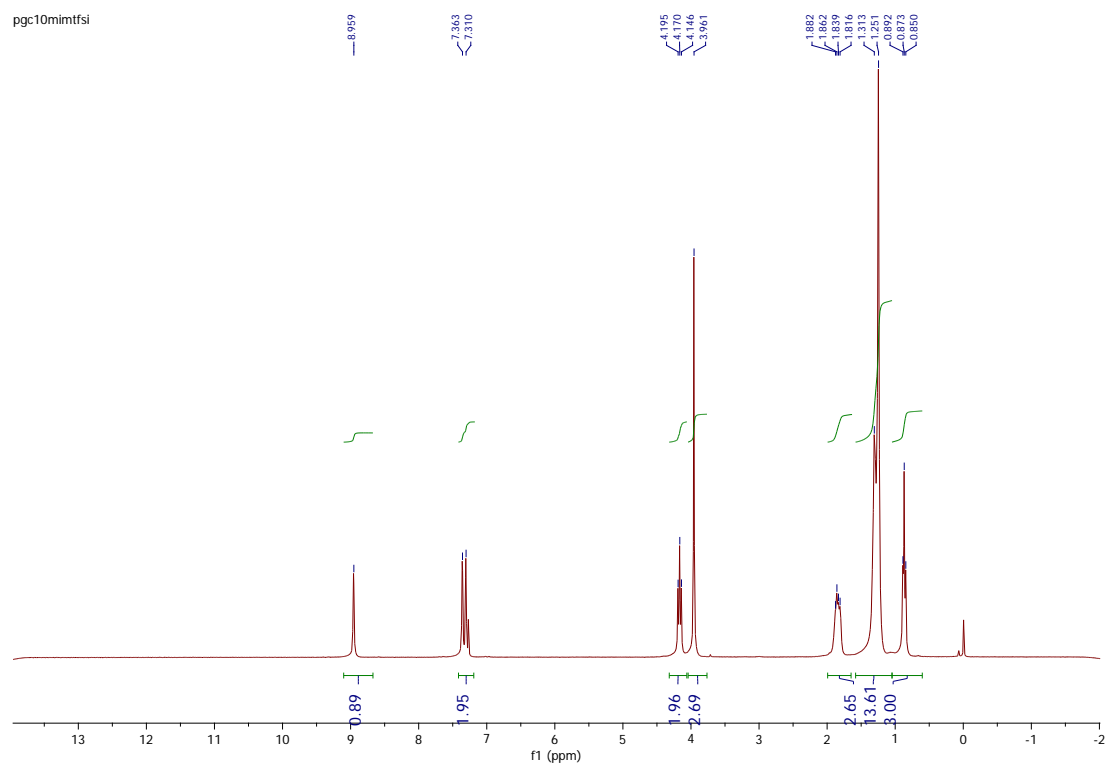
**Figure S4.**  $^1\text{H}$ -NMR of  $[\text{C}_6\text{mim}][\text{NTf}_2]$  in  $\text{d}_6$ -DMSO.



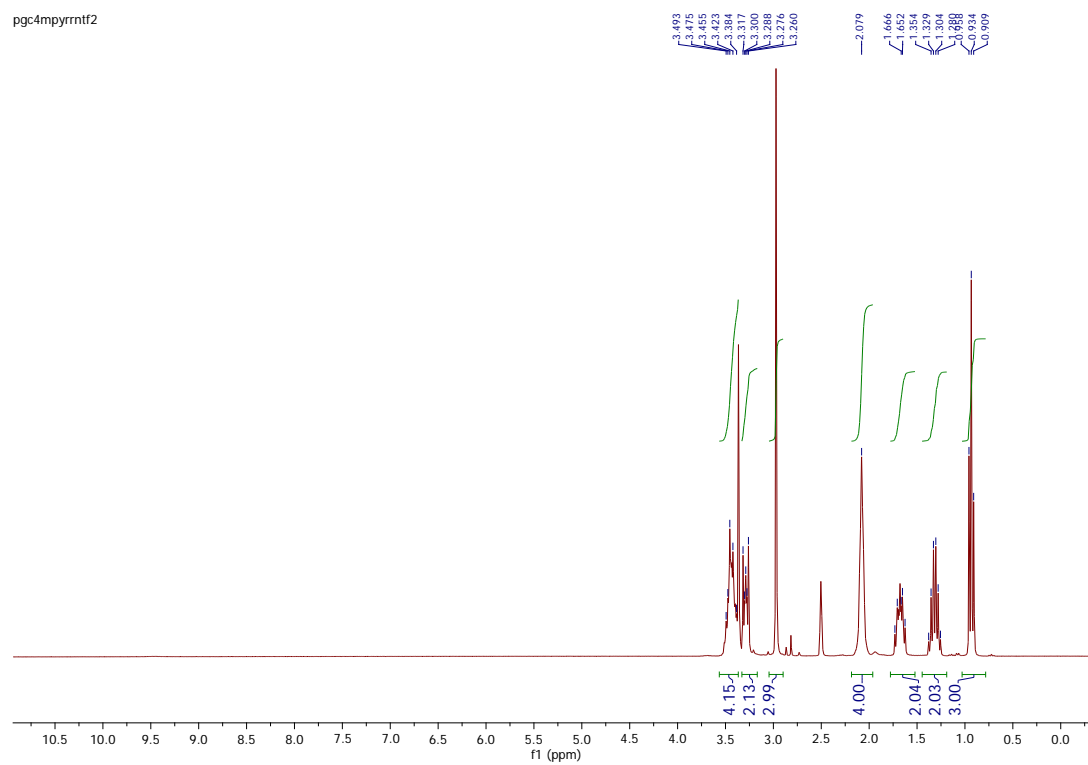
**Figure S5.**  $^1\text{H}$ -NMR of  $[\text{C}_8\text{mim}][\text{NTf}_2]$  in  $\text{CDCl}_3$ .



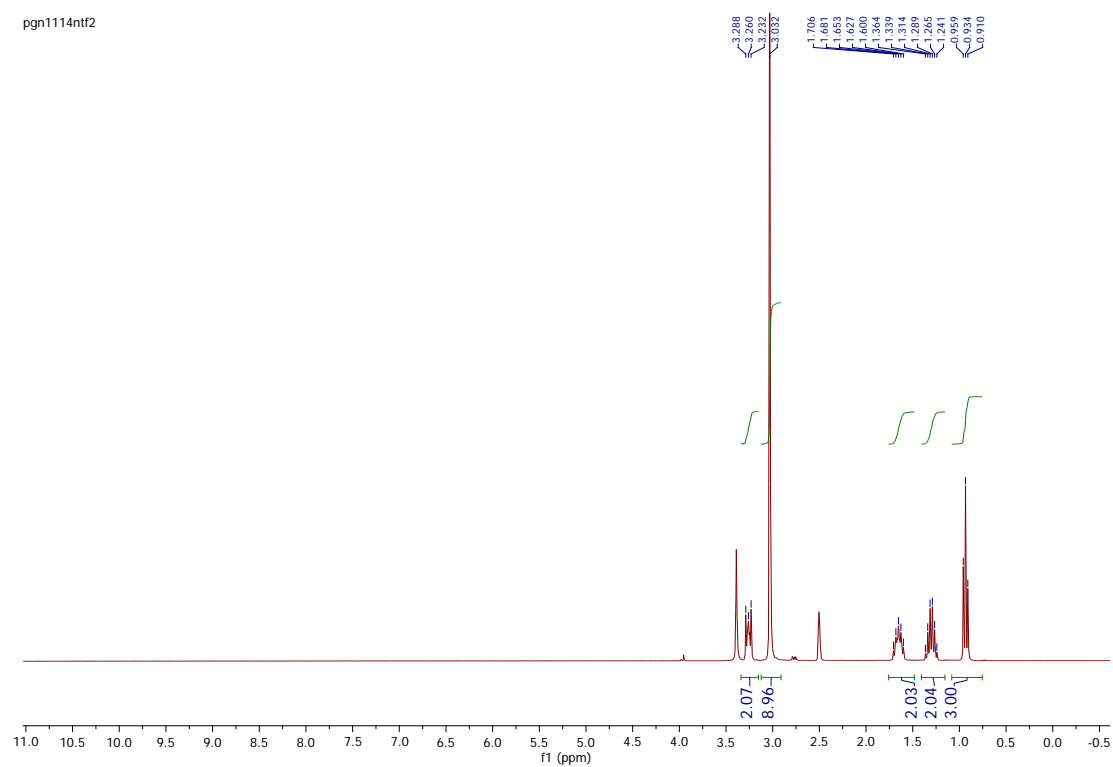
**Figure S6.**  $^1\text{H}$ -NMR of  $[\text{C}_{10}\text{mim}][\text{NTf}_2]$  in  $\text{CDCl}_3$ .



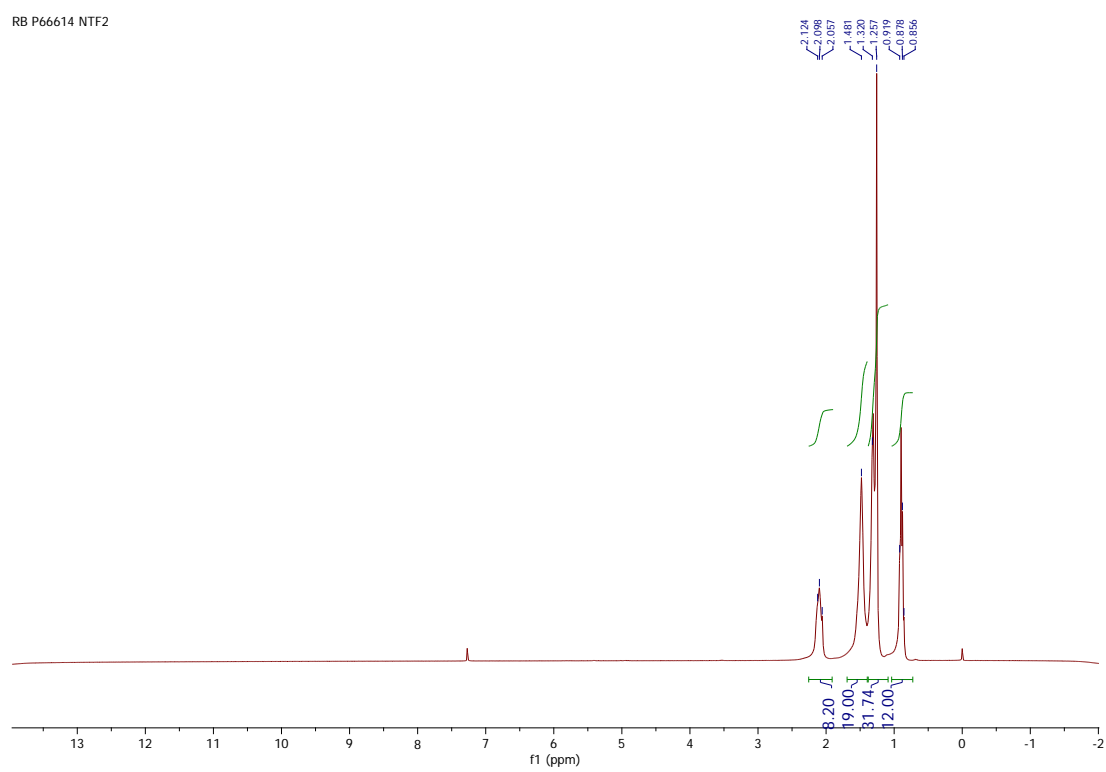
**Figure S7.**  $^1\text{H}$ -NMR of  $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$  in  $\text{d}_6$ -DMSO.



**Figure S8.**  $^1\text{H}$ -NMR of  $[\text{N}_{1114}][\text{NTf}_2]$  in  $\text{d}_6$ -DMSO.

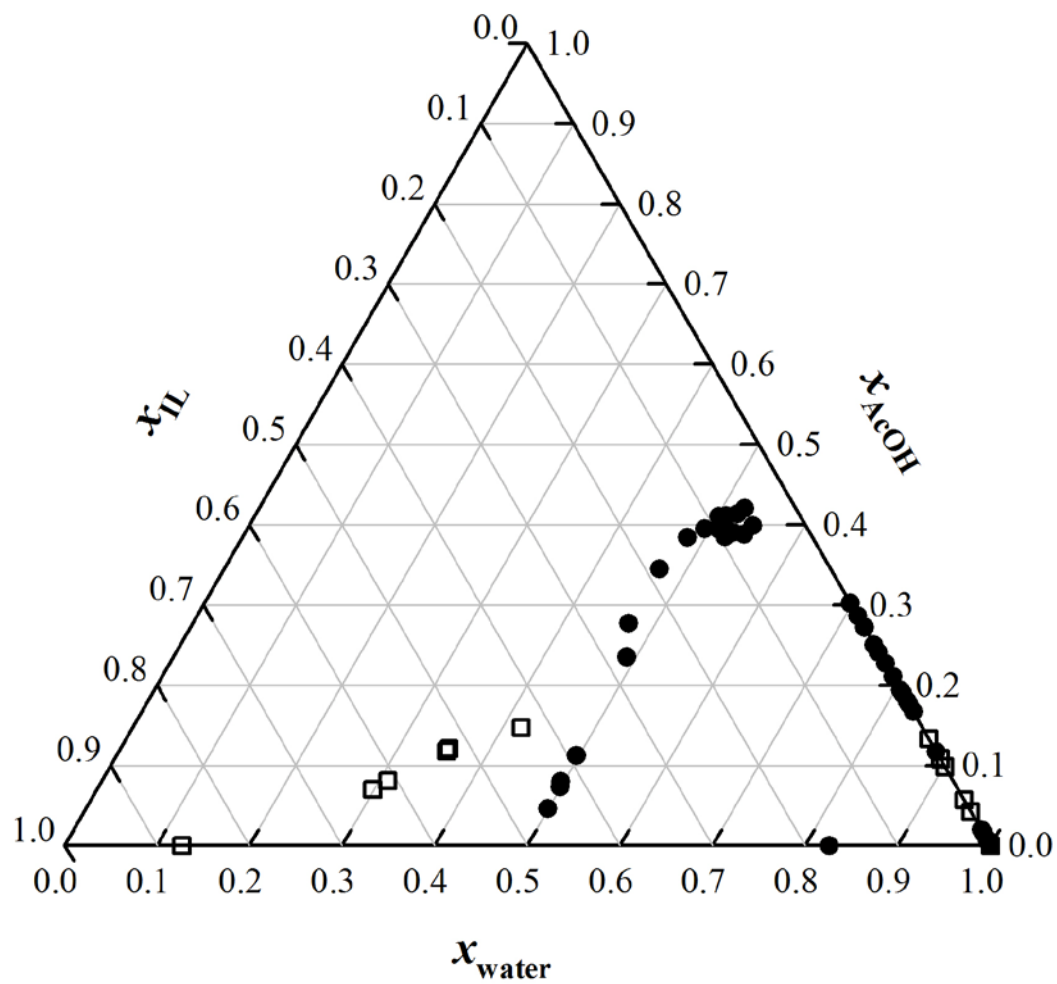


**Figure S9.**  $^1\text{H}$ -NMR of  $[\text{P}_{66614}][\text{NTf}_2]$  in  $\text{CDCl}_3$ .

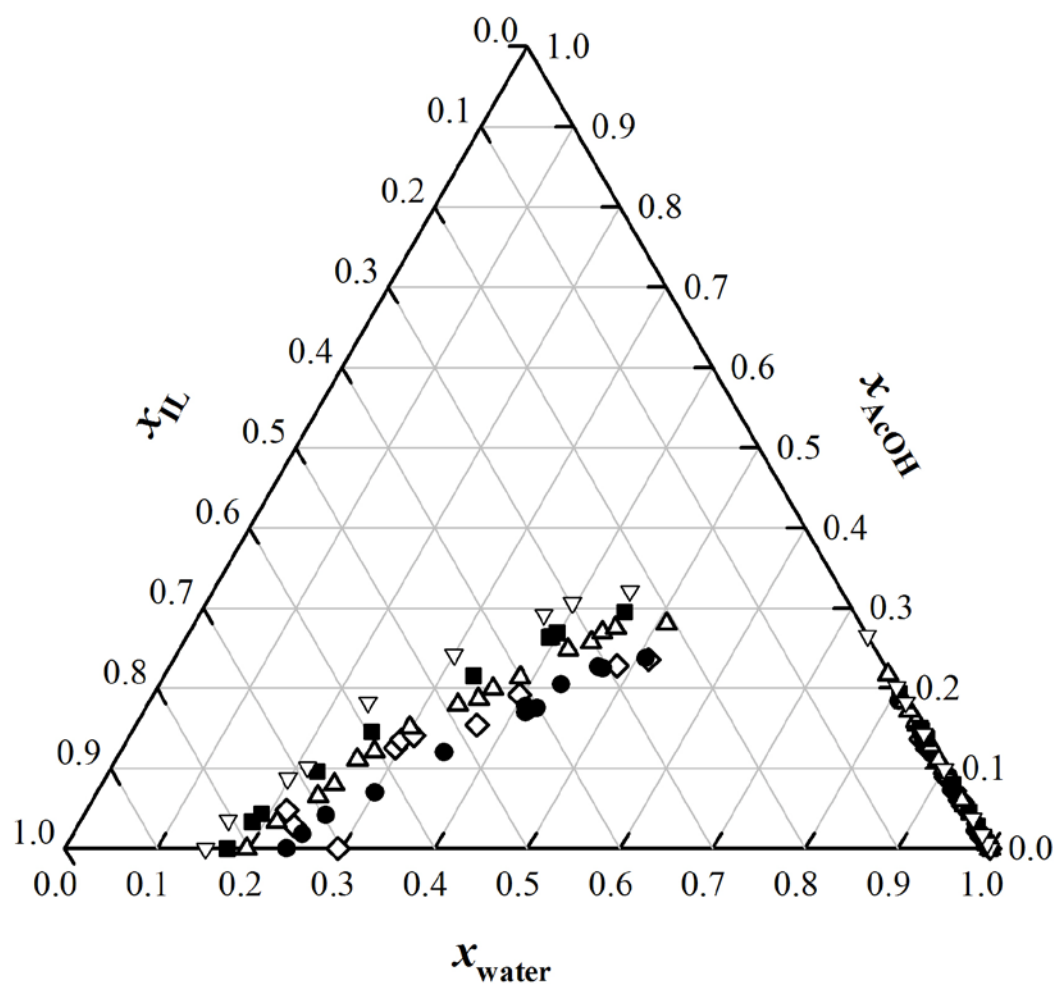




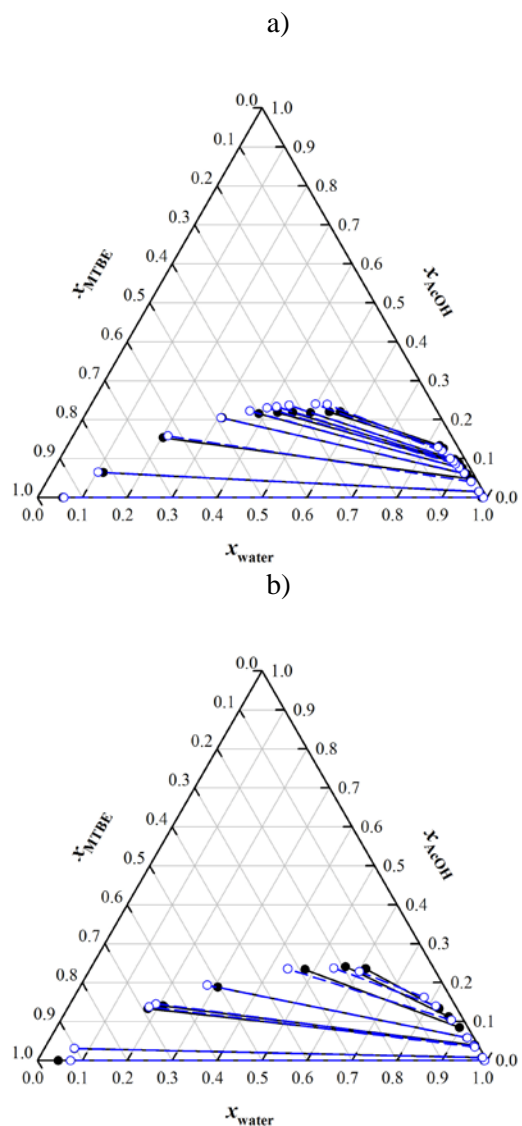
**Figure S10.** Equilibrium diagram of the ternary system (water + acetic acid + IL) at 293.15 K and at 101 kPa: ●, [P<sub>666,14</sub>]Cl; □, [P<sub>666,14</sub>][NTf<sub>2</sub>].



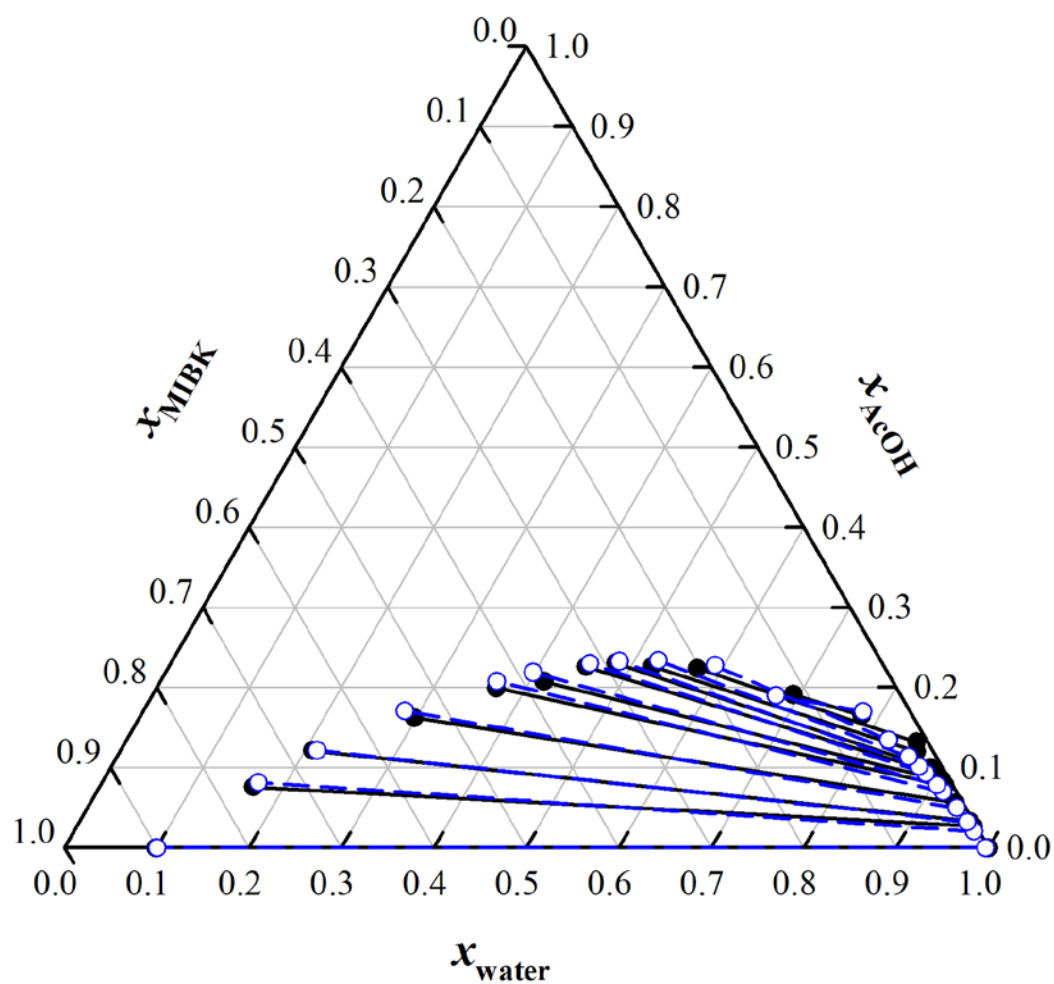
**Figure S11.** Equilibrium diagram of the ternary system (water + acetic acid +  $[C_n\text{mim}][\text{NTf}_2]$ ) at 293.15 K and at 101 kPa:  $\diamond$ ,  $n = 2$ ;  $\bullet$ ,  $n = 4$ ;  $\triangle$ ,  $n = 6$ ;  $\blacksquare$ ,  $n = 8$ ;  $\nabla$ ,  $n = 10$ .



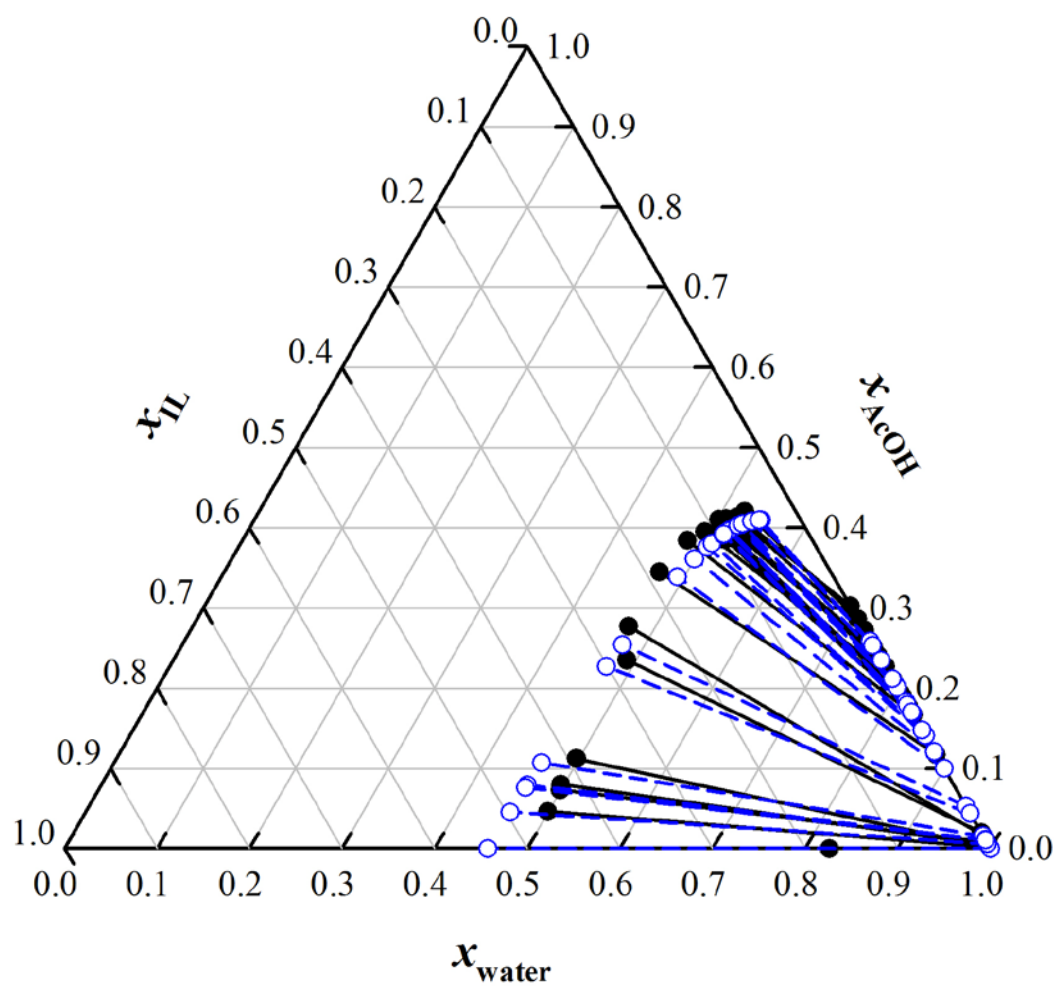
**Figure S12.** Equilibrium diagram of the ternary system (water + acetic acid + MTBE) at 101 kPa and at: a, 293.15 K; b, 313.15 K; (● and solid lines), experimental data; (○ and dashed lines), predicted using UNIQUAC model with parameters from Miao *et al.*<sup>15</sup>



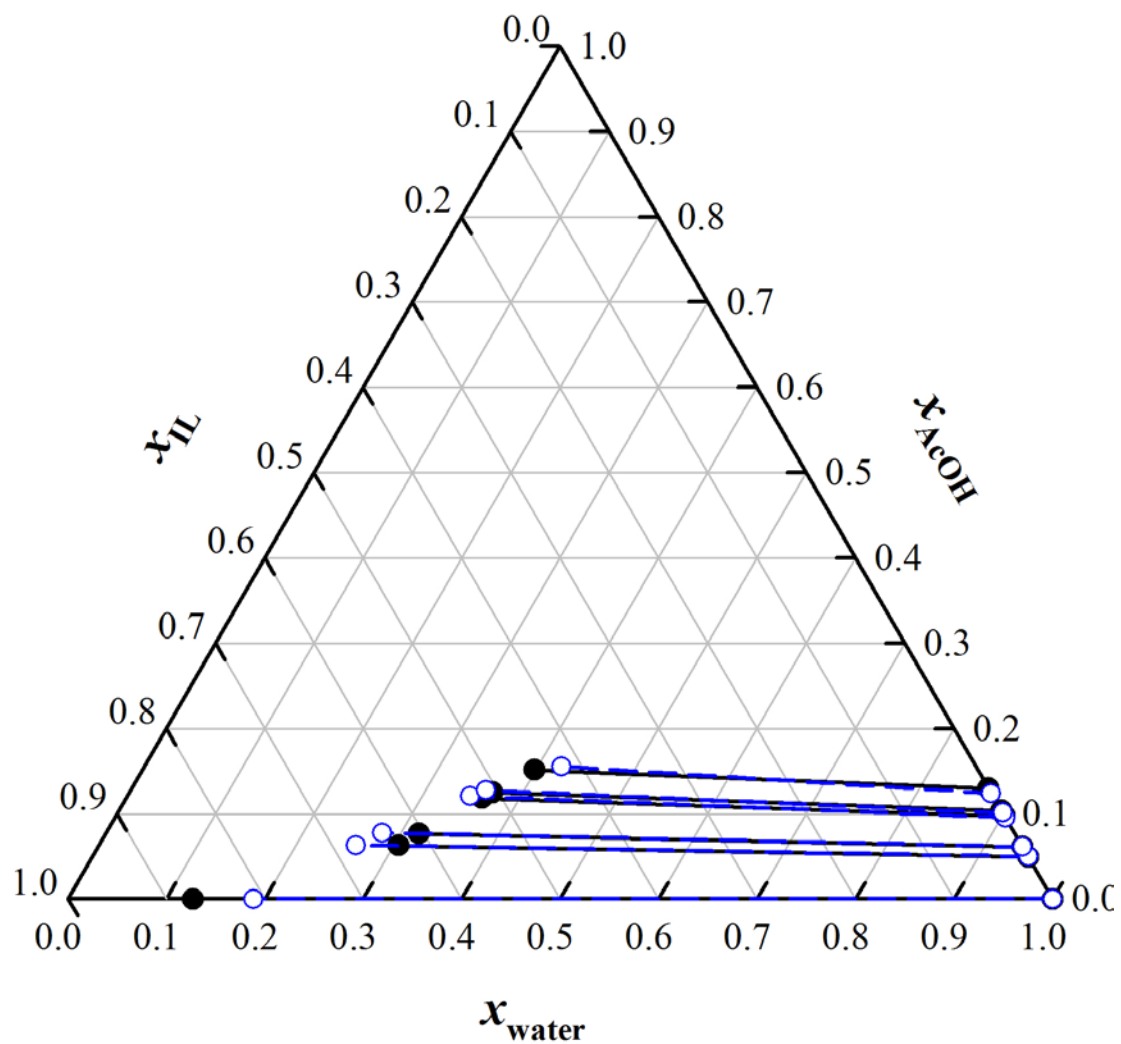
**Figure S13.** Equilibrium diagram of the ternary system (water + acetic acid + MIBK) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



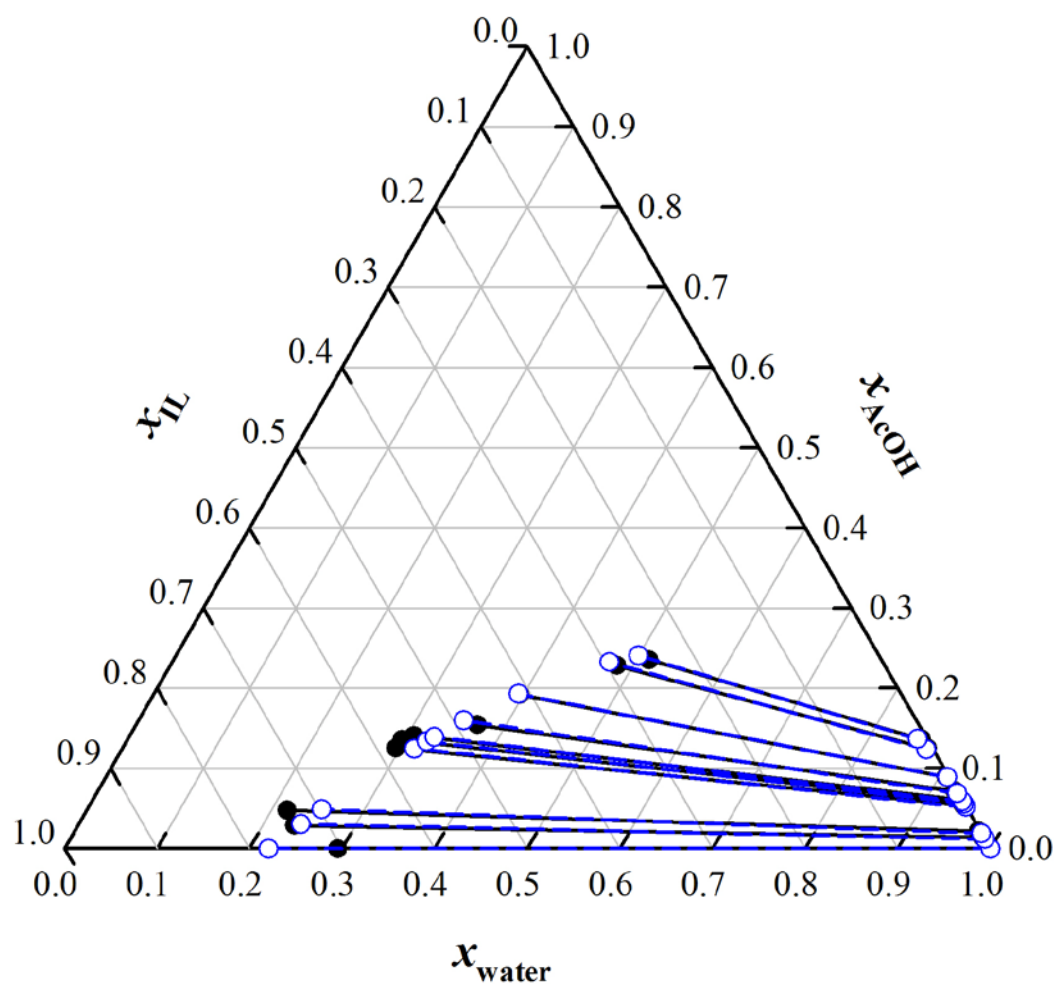
**Figure S14.** Equilibrium diagram of the ternary system (water + acetic acid +  $[P_{666,14}]\text{Cl}$ ) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



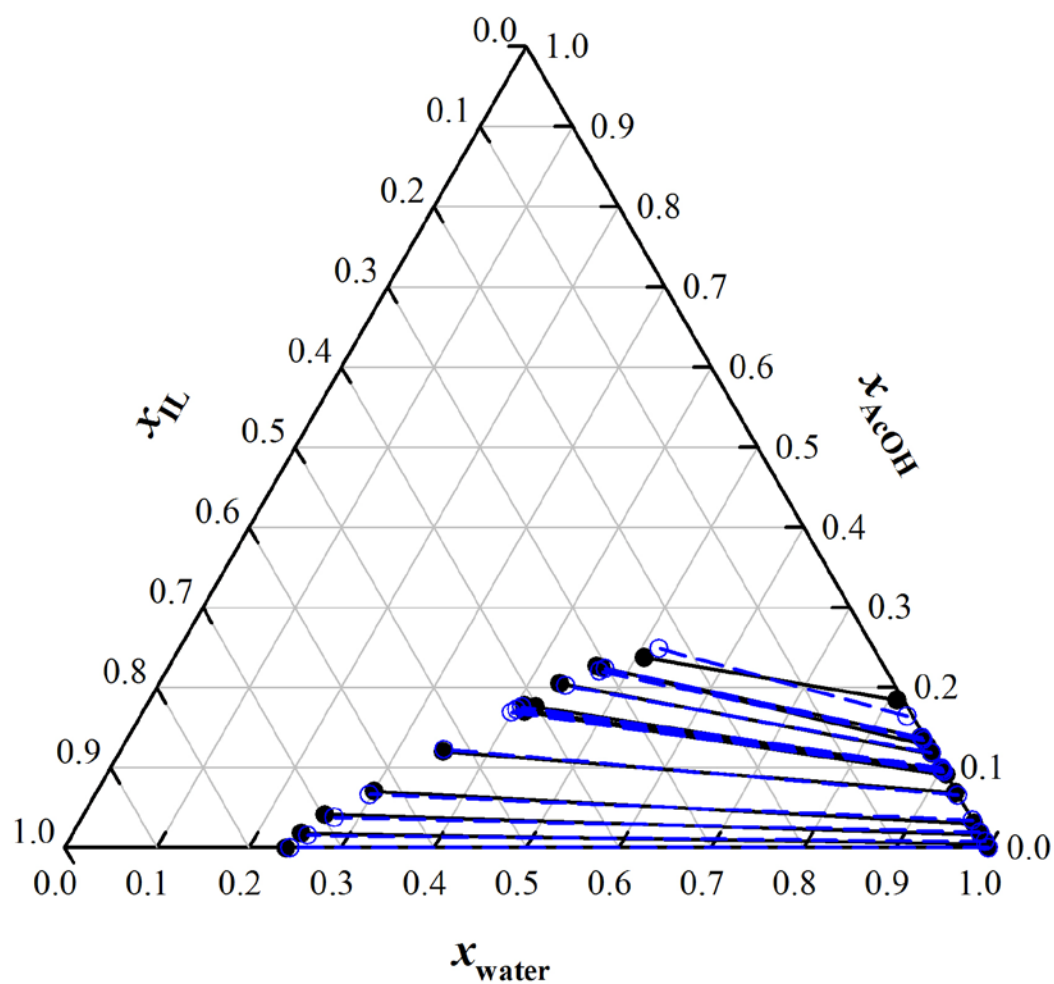
**Figure S15.** Equilibrium diagram of the ternary system (water + acetic acid + [P<sub>666,14</sub>][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



**Figure S16.** Equilibrium diagram of the ternary system (water + acetic acid + [C<sub>2</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

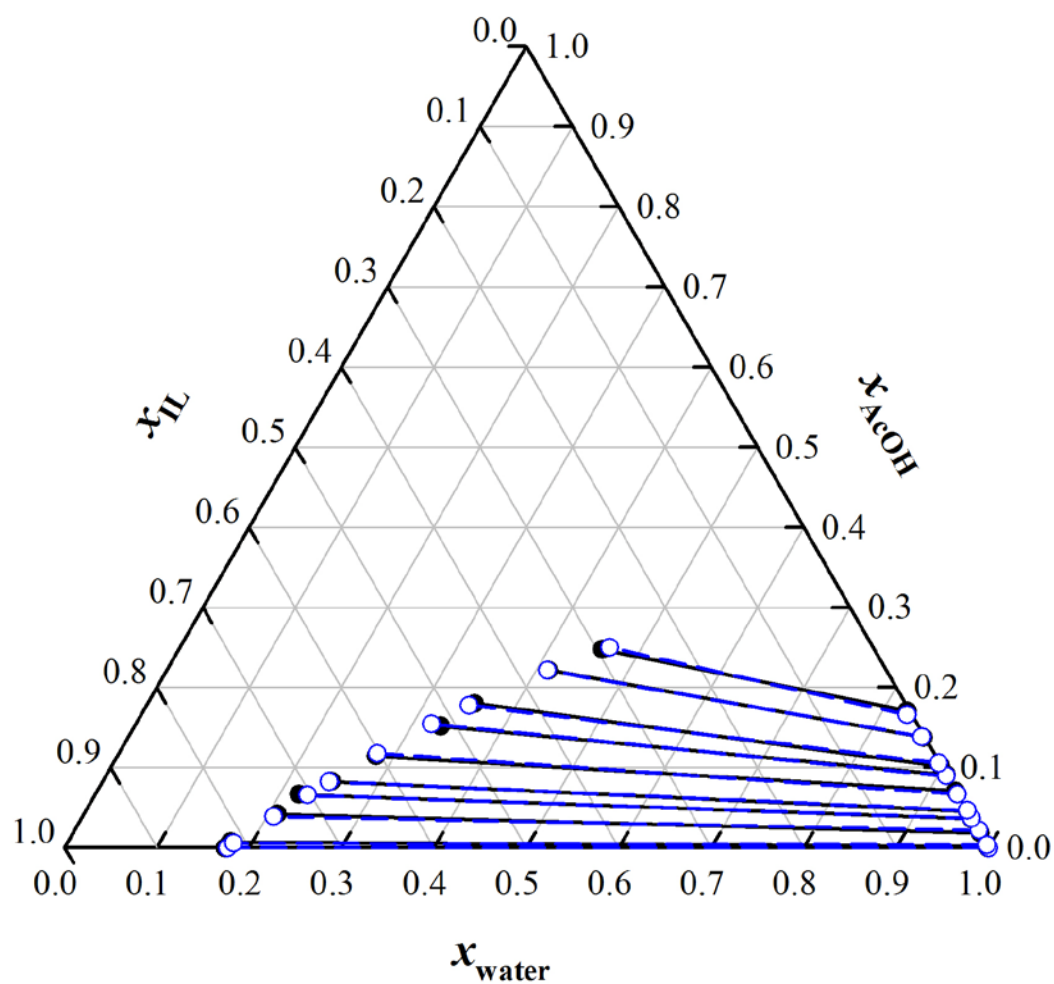


**Figure S17.** Equilibrium diagram of the ternary system (water + acetic acid + [C<sub>4</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.

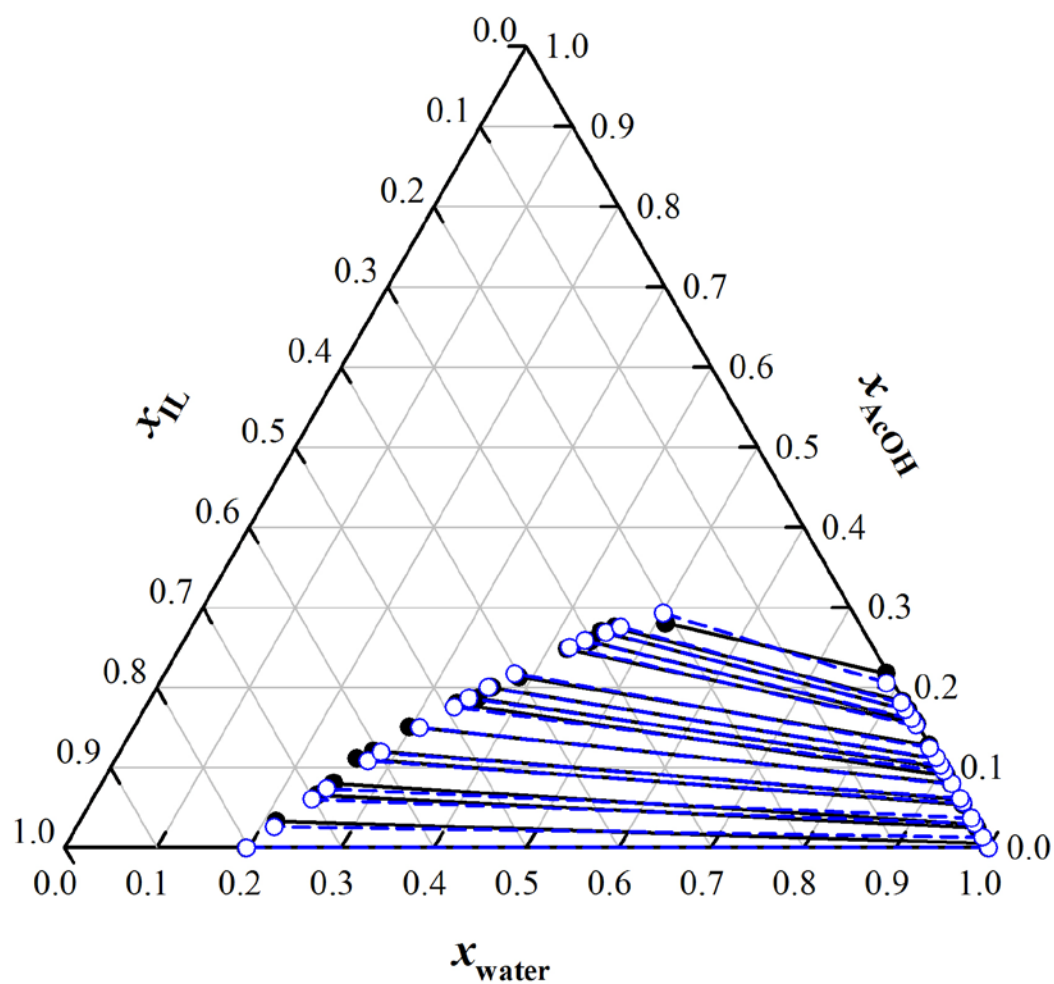




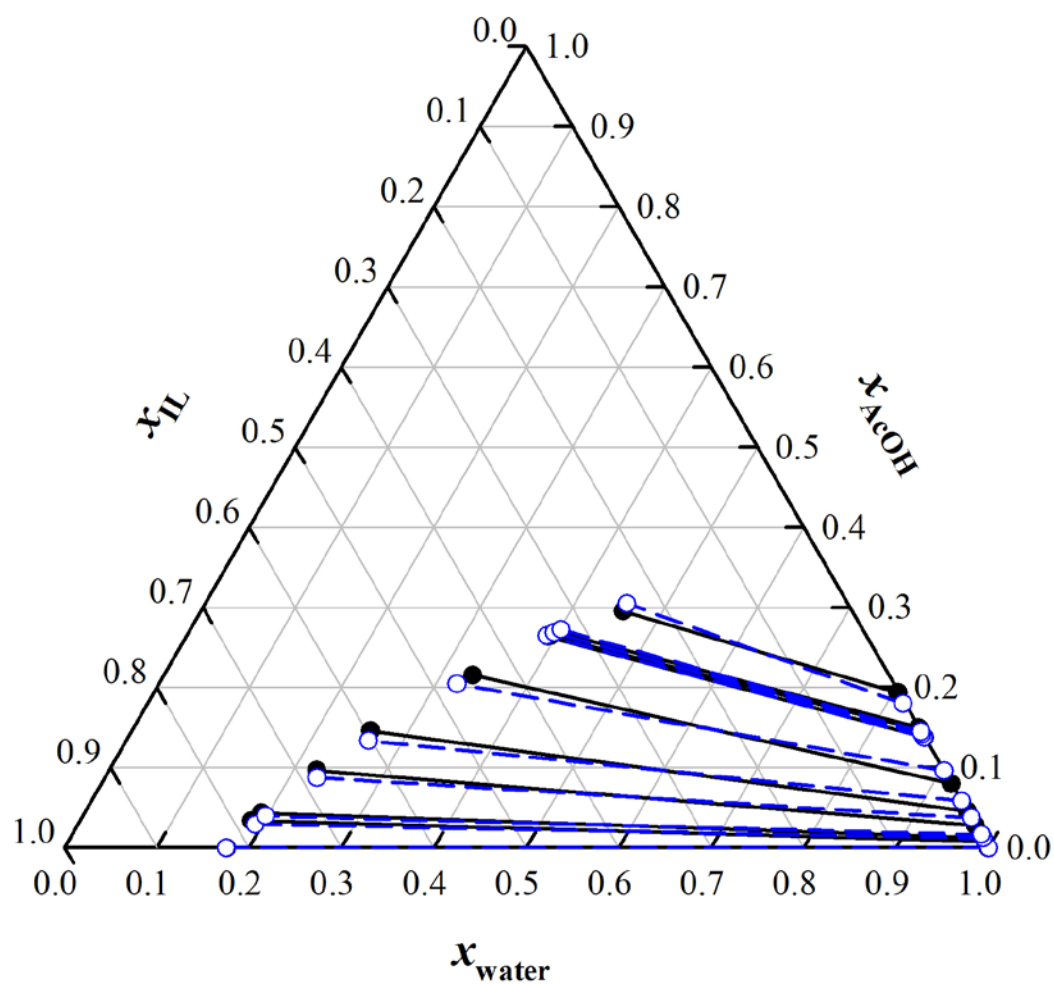
**Figure S18.** Equilibrium diagram of the ternary system (water + acetic acid + [C<sub>4</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



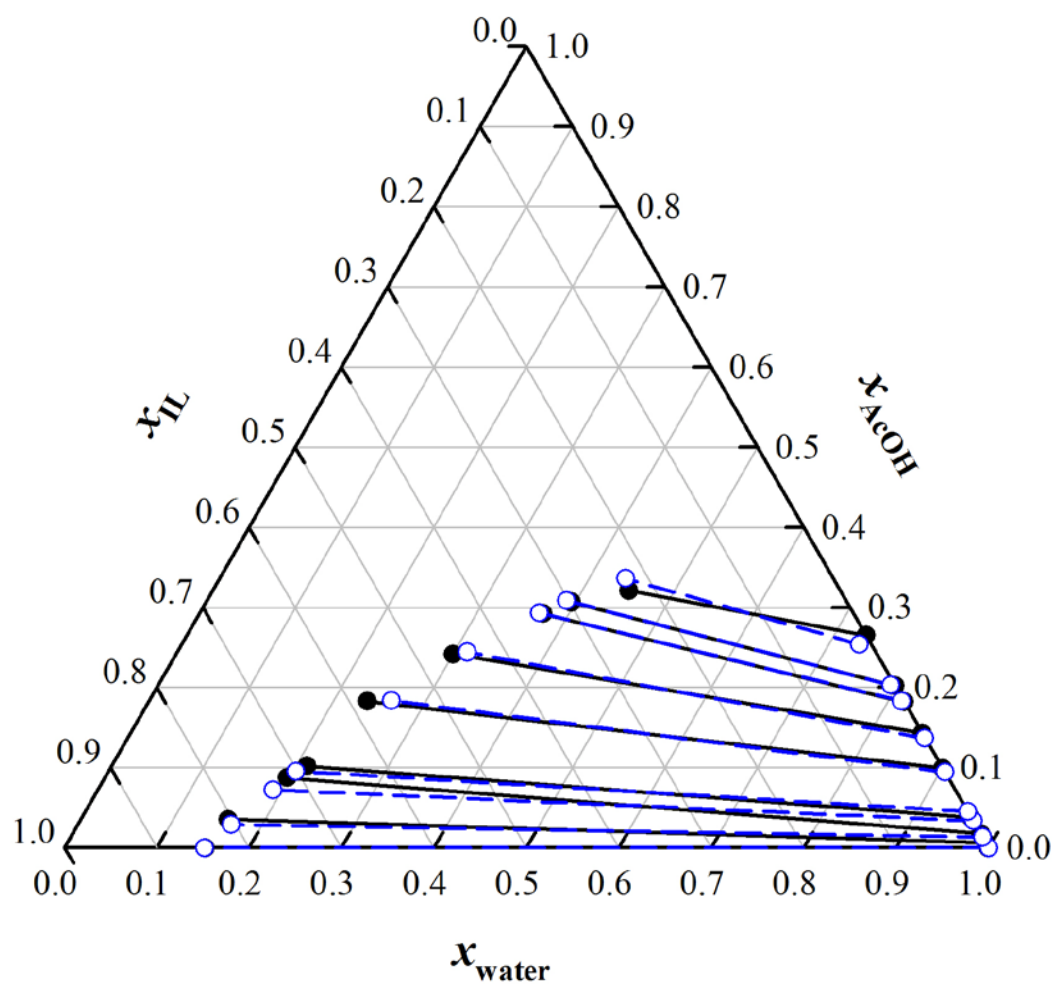
**Figure S19.** Equilibrium diagram of the ternary system (water + acetic acid + [C<sub>6</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



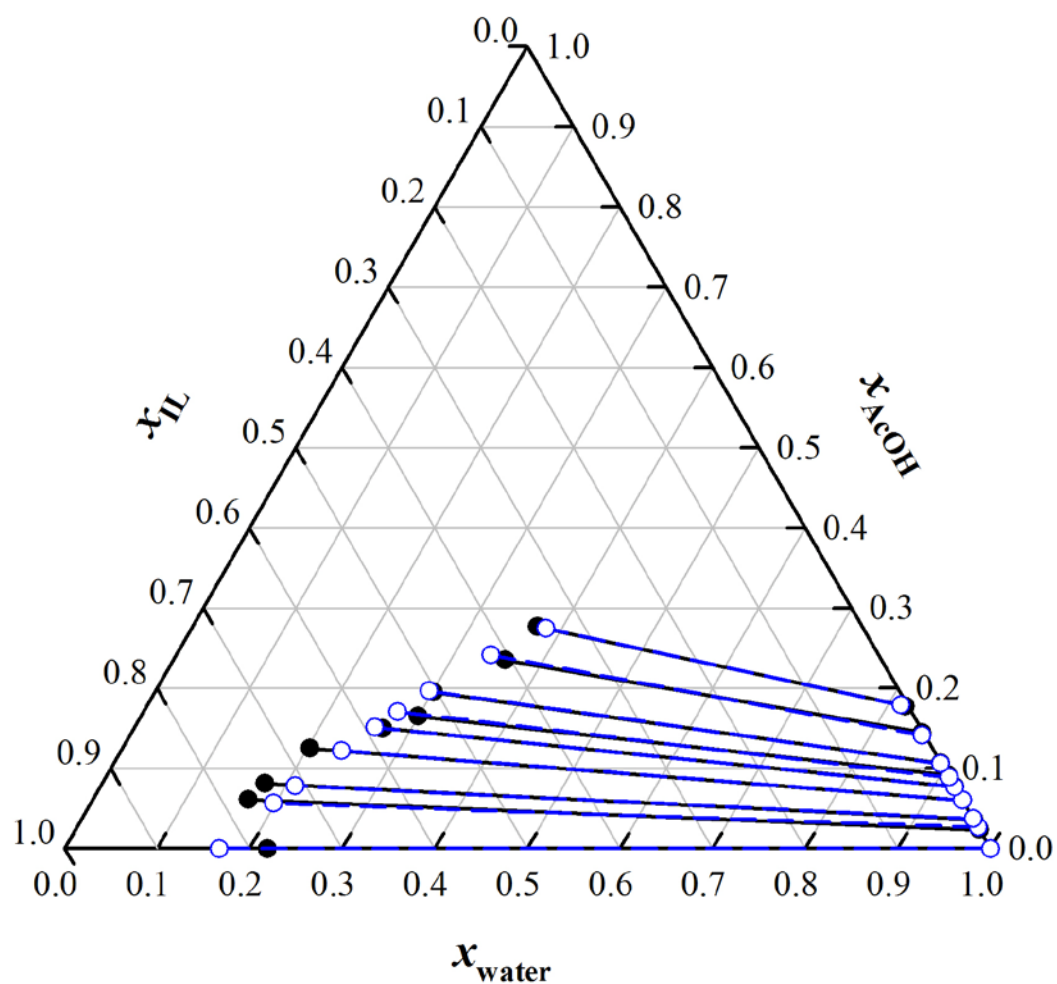
**Figure S20.** Equilibrium diagram of the ternary system (water + acetic acid + [C<sub>8</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



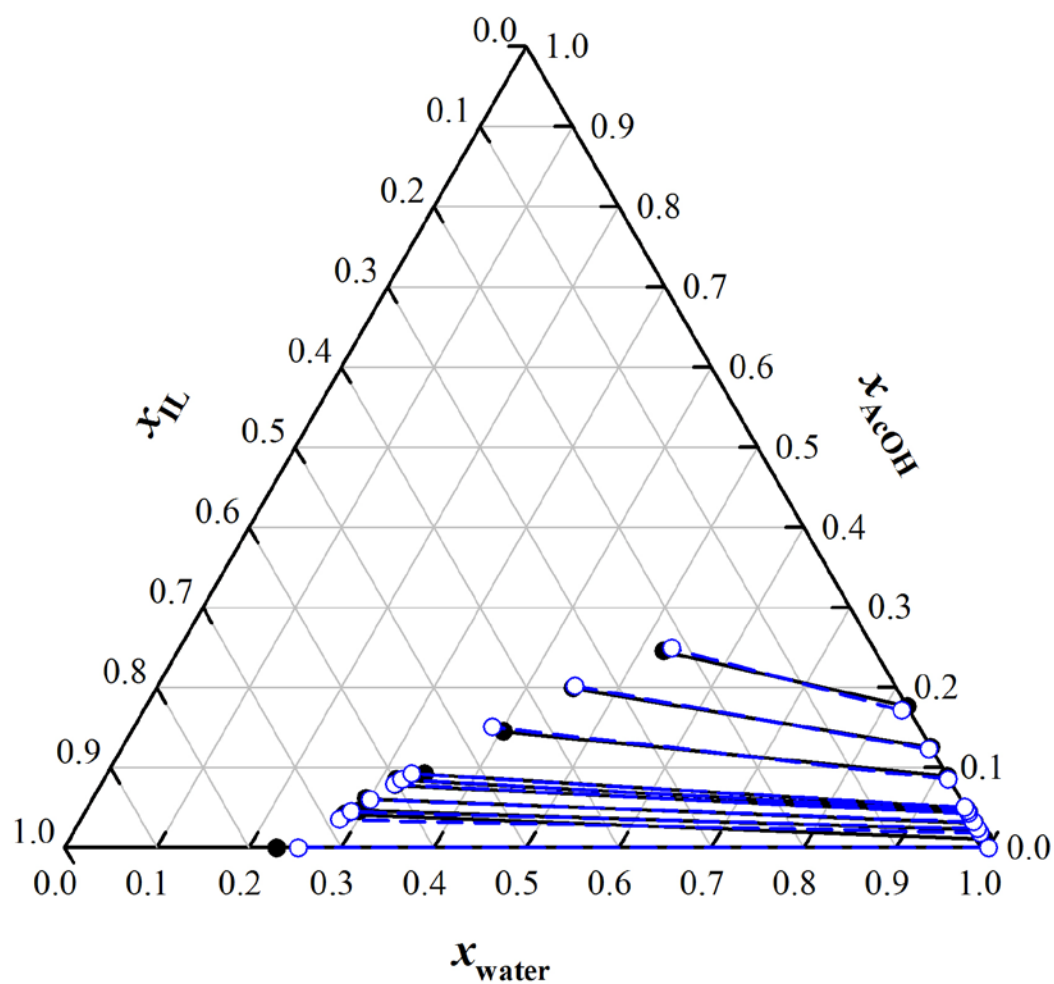
**Figure S21.** Equilibrium diagram of the ternary system (water + acetic acid + [C<sub>10</sub>mim][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



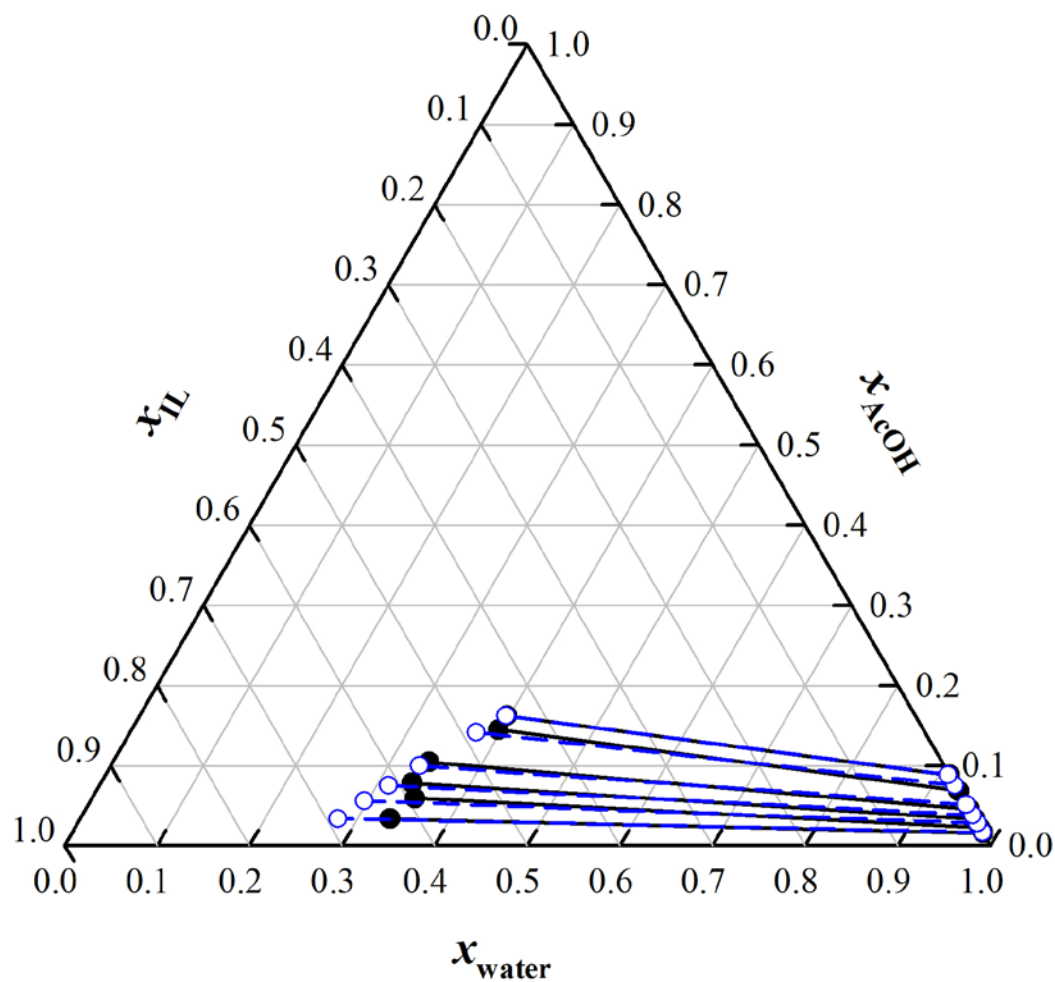
**Figure S22.** Equilibrium diagram of the ternary system (water + acetic acid + [C<sub>4</sub>mpyrr][NTf<sub>2</sub>]) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



**Figure S23.** Equilibrium diagram of the ternary system (water + acetic acid +  $[\text{N}_{1114}][\text{NTf}_2]$ ) at 293.15 K and at 101 kPa: (● and solid lines), experimental data; (○ and dashed lines), correlated using UNIQUAC model.



**Figure S24.** Equilibrium diagram of the ternary system (water + acetic acid + [C<sub>4</sub>mim][NTf<sub>2</sub>]) at 298.15 K and at 101 kPa: (● and solid lines), experimental data from Bharti and Banerjee;<sup>16</sup> (○ and dashed lines), predicted using UNIQUAC model with parameters reported during this work.



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